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Prospects of applying ionic liquids and deep eutectic solvents for renewable energy storage by means of redox flow batteries

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A B S T R A C T

Ionic liquids (ILs) and deep eutectic solvents (DESs) have been applied in various fields such as electrolytes for lithium ion batteries, electrodeposition, electropolishing and even in fuel cells. ILs and molten salts have found some applications in redox flow batteries (RFBs) in the past and recently some metal ion based ILs have been proposed and used by Sandia National Laboratories. In addition, only two papers have very recently reported on the application of DESs for the same. This review gives an overview on DESs and discusses the possibility of employing them in RFBs for renewable energy storage and utility-scale load leveling applications. Commencing with a discussion on energy storage technologies and the RFB, this paper goes on to provide an account on ILs and DESs as well as their applications in electrochemistry and energy conversion. A succinct discussion on the results of Sandia National Laboratories on using ILs as electrolytes for RFBs is provided building onto the feasibility of replacing ILs with DESs in the near future (based upon recent publications on the topic).

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1. Introduction

Efficient renewable energy storage needs to accumulate energy during times when demand is low (peak shaving) and to supply it

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when demand is high in order to ensure efficient energy handling (load leveling) [1]. A number of technologies based on electrical, chemical, electrochemical and mechanical processes have been proposed to address the energy storage needs of electrical grids [1–6]. Electrochemical storage systems are found to be robust due to their relative ease of siting as well as fast response times [1].

Electrochemical energy storage systems provide direct conversion between chemical and electrical energy and are therefore particularly suited to the storage of the latter [1]. Electrochemical storage technologies also offer additional advantages compared with other types of energy storage systems, including [7]:

- Modularity whereby they can be used in applications ranging from a few kWh to several MWh.
- Simultaneous application for both power quality and energy management.
- Low environmental impact, which means they can be sited near residential areas.

Redox flow batteries (RFBs) are rechargeable electrochemical systems that rely on the redox states of various soluble species for the purposes of storing and releasing energy via highly efficient charge/discharge processes [8–10]. The redox flow cell concept can be traced back to the zinc/chlorine system that was developed in 1884 by Charles Renard and Arthur Krebs to power their army airship “La France” (a historical timeline for the development of RFBs is shown in Fig. 1) [11,12]. The concept was then re-visited by Posner in the mid-1950s [12] prior to an independent investigation that was conducted in Japan around 1968 [2,13]. The modern iron/chromium RFB was invented by Lawrence Thaller at the National Aeronautics and Space Administration (NASA) in the USA [13–15]. Since then, the technology has been developed significantly leading to many small to medium-scale field tests and demonstrations in the last two decades [16]. As fully soluble redox couples and inert electrodes are used (Fig. 2) [1,7,9,13,17], undesirable electrode processes are eliminated (especially structural changes of the electrode) in comparison to secondary battery systems [1,18]. The system energy storage capacity is determined by the concentrations of the reactants and the size of the storage tanks, while the system power is determined by the number of individual cells within a battery stack and their electrode area [19]. As a result it is possible to independently optimize the flow cell′s storage capacity and power output [1]. This feature makes RFBs unique in their ability to provide the specific power and energy requirement for each application. Storage capacity can be increased by adding more electrolytes, so the incremental cost of each additional energy storage capacity unit is lower than that of other types of batteries [7]. The cost per kWh of the system therefore decreases substantially with increasing storage capacity, making the RFB particularly attractive for applications requiring storage times in excess of 4–6 h [1].

One of the key factors limiting the widespread commercialization of RFBs appears to be their low energy density. One means of overcoming this drawback has been the employment of non-aqueous electrolyte solvents that can offer a wide potential window of operation and increase the energy capacity of the system [20–25]. Nonetheless, the organic systems used so far have limited availability (thereby affecting their cost) and are also not environmentally friendly [1,22]. Therefore a new class of non-aqueous electrolytes has been considered for energy storage applications and is popularly known as ionic liquids (ILs) [26–30]. This also has limitations due to its high cost and its electrochemistry can be severely affected in the presence of water [31]. This can be avoided if deep eutectic solvents (DES) are employed in the place of ILs [32].

The aim of this paper is to stimulate interest within the scientific community to explore the application of ILs and DESs in various RFB configurations. Recently, Sandia National Laboratories [4] and Tianjin

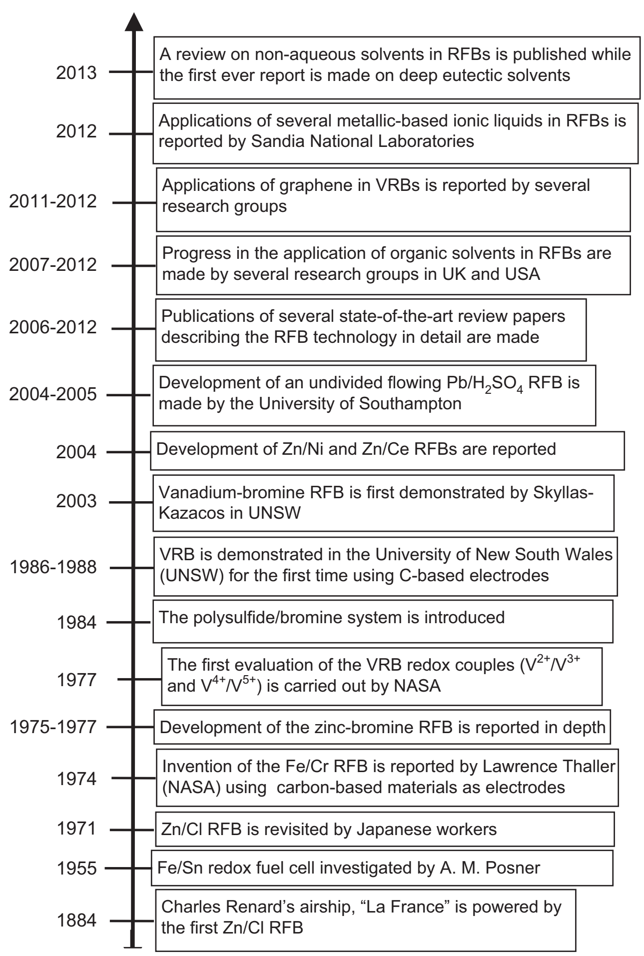


Fig. 1. Timeline for the development of RFBs.
Adapted from Walsh and co-workers [7].

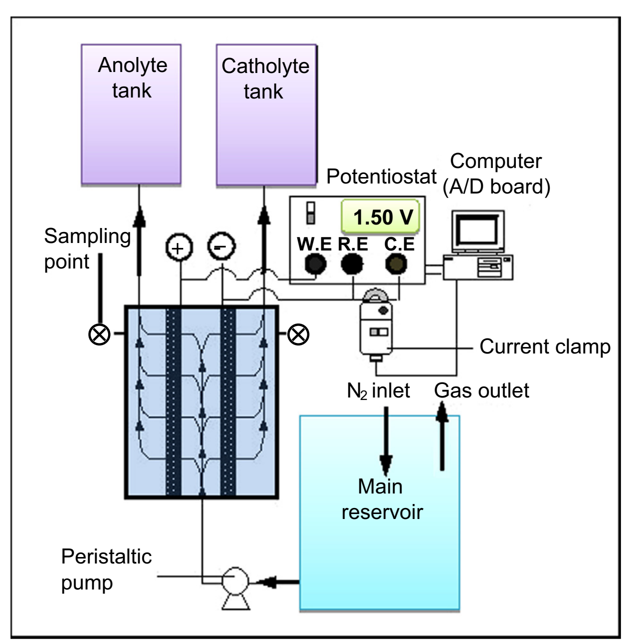


Fig. 2. Schematic diagram of a redox flow battery reactor.
Reproduced with permission from the Electrochemical Society [1,7,9,13,17].

University [33] have reported some results on the use of ILs as electrolytes for RFBs. However, there are few reports on the employment of DESs in RFBs to date. Therefore the prospects of applying DESs in RFBs is discussed below using results reported in the literature on the Electrochemical Engineering aspects of these solvents.

2. Overview on renewable energy storage

Renewable energy has been growing in demand throughout the world due to environmental issues such as global warming or acid rain. These problems have resulted due to an excessive use of fossil fuels as a consequence of unprecedented growth in agricultural, domestic and industrial activities especially in emergent countries [34,35]. In response, there are strong possibilities of replacing fossil fuels with renewable sources of energy in the future due to their significantly lesser impact upon the environment [36]. Renewable energy also presents important drawbacks, such as the discontinuity of generation, as most resources depend on climatic conditions [37–39]. Despite that, combining these renewable energy sources with back-up units to form a hybrid system can provide a more economic, environment friendly and reliable supply of electricity in comparison to the single-usage of such systems [40].

Another alternative means of improving the sustained supply of the renewable and yet intermittent energy involves the design and deployment of efficient energy storage technologies [1,7,41,42]. Each technology has some inherent disadvantages that make it practical or economical for only a limited range of applications [43]. When combining performance requirements with cost, electrochemical systems are seen to be superior to the other forms of energy storage which are mainly mechanical in nature and therefore have relatively longer response times (Table 1) [1,7].

A redox flow battery (RFB) is a promising large scale energy storage device which utilizes oxidation and reduction reactions of two redox couples in the electrolytes for charge and discharge (Fig. 2) [1,7,9,13,44]. Electrical energy is stored in the electrolytes, which are reserved in two separate containers. The electrolytes are pumped into an electrochemical reactor where the reactions occur in two chambers separated by a membrane [7,33].

RFB technologies have demonstrated their ability to provide large-scale energy storage for applications including remote area power supplies (RAPS), back-up power supplies, distributed power generation and power quality optimization [45]. Although most of these applications are at the kW power scale, both MW- and GW-scale stationary batteries have the potential to contribute to (1) improved energy efficiency and flexibility of national electricity grids, through load leveling/peak shaving, and (2) grid stabilization of power derived from renewable energy-based sources [16]. For example, the all-vanadium battery has already been trialed or adopted commercially for load leveling and/or renewables support in Australia [1], Austria [46], Canada [47], Germany [48], China [49], the Republic of South Africa (RSA) [50], South East Asia [1], the United States of America (USA) [45], and, especially, Japan [51]. Table 2 provides a summary of the various trials of the vanadium RFB for applications ranging from kW to MW scales [45]. The economic and environmental benefits of the vanadium RFB installed at King Island in 2003 are summarized in Table 3. This simple, non-annuitized economic analysis yielded an estimated 3.5-year payback period for the return of the capital investment in terms of reducing operational costs relative to the running of a diesel-fuelled generator. Using these projected emissions reductions (Table 3) and assuming that a similar unit could be installed in Europe (included, for example, in the EU Emission Trading Scheme), 4 kton of avoided carbon-based emissions could alone be traded at €48,000 (≈ $67,000) yr^{-1} (assuming an allowance of €12 $[CO_2]$ ton^{-1}).

Table 1
Comparison of performance requirements with costs for different energy storage technologies.
Reproduced with permission from the Electrochemical Society [1].

Energy storage	Power rating (MW)	Discharge duration (h)	Response time	Efficiency (%)	Capital Cost ($/kWh)	Cycle Cost ($/kWh) output	Life (yr)	Cycle life at 80% depth of discharge	Maturity	Safety issues	Limitations
PHES	10's–1000's	> 8	Very good	70–85	80–200	0.001–0.02	30	20,000–50,000	Commercial	Exclusion area	Special geological and geographic requirements
SMES	10's	0.25	Good	90–95	10,000	0.4–1.70	30	1000–10,000	Commercial	Magnetic field	Long loop for useful storage
CAES	10's–1000's	0.1–15	Very good	60–79	50–110	0.03–0.06	30	9000–30,000	Demonstration stage	Pressure vessels	Special geological and geographic requirements
FES	0.001–0.1	0.1–1	Slow	> 90	300–5000	0.05–0.4	20	> 20,000	Commercial	Containment	Low energy density and efficiency
SES	0.005–0.1	0.02–1	Good	> 95	82,000	0.03–0.4	Low	10,000–100,000	Almost commercial	–	Low energy density and high self-discharge
TES	1–100's	1–45	Slow	60	500	0.035–0.16	20	4000–10,000	Commercial	High temperature	Large investments
LAB	0.001–10	0.1–4	Fast	70–76	350–1500	0.40–1	5–10	200–1500	Several MW scale demonstrations	Potential for hydrogen explosions	Low to medium energy density. Poor deep discharge performance
SSB	0.1–100's	1–10	Fast	85–90	300–950	0.09–0.5	5–10	210–4500	Multi-kW to MW scale demonstrations	High temperature operation.	Poor thermal cycling
LIB	0.001–100	0.1–1	Fast	> 90	850–5000	0.3–1	5–10	5000–7000	Several MW-scale demonstrations	Potential fires and explosions	High cost
RFB	0.001–100	1–20	High	75–85	180–250	0.06–0.2	> 10	5000–14,000	More than 20 multi-kW to MW scale demonstrations.	Chemical handling and leakage	Low to medium energy density. Require more parts when compared to other batteries

PHES = Pumped hydro energy storage; SMES = superconducting energy storage; CAES = compressed air energy storage; FES = flywheel energy storage; SES = supercapacitor energy storage; TES = thermal energy storage; LAB = lead acid battery; SSB = sodium sulfur battery; LIB = lithium ion battery; RFB = redox flow battery.

Table 2
Summary of performance of the all-vanadium RFB at the 1 kW–1 MW-scale (renewable energy level). η_E=energy efficiency of flow battery stack; η_{system}=total system power efficiency.
Reproduced with permission from Wiley [45].

No.	η_E	Power	Energy	Country	Funding body
1	Not stated	1 kW	5 kW h	Australia	Australian Department of Resources and Energy
2	72–90%	1.33 kW	0.7 kW h (40–42 A h)	Australia	Australian National Energy Research Development Council, NSW Department of Minerals & Energy and Mount Resources Ltd.
3	Not stated	1.6–5 kW	12 kW h	Australia	Australia Research Council, Pacific Power, NSW Office of Energy and Thai Gypsum Co. Ltd.
4	> 80% 80% 80–85%	1–3 kW ≈ 20 kW	Not stated ≈ 10 kW h (0.5 h)	Australia	Unisearch Ltd.
5	η_{system}=80–85% 75–82% η_{system}=70%	50 kW 450 kW	175–400 kWh 900 kW h (2 h)	Japan	Sumitomo Electric Ltd. and The Kansai Electric Power Co., Inc.
6	Not stated	200 kW	800 kW h (4 h)	Japan	Kashima-Kita Electric Power Corp.
7	Not stated	Not stated	30–3 MW h	Japan	Sumitomo Electric Ltd. and The Kansai Electric Power Co., Inc.
8	Not stated	10–50 kW	Not stated	Thailand	Cellennium (Thailand) Company Ltd.
9	82–85%	250 kW	520 kW h	Australia/Canada	Telepower Australia Pty. and Vanteck (VRB) Technology Corp.
10	Not stated	1.5 MW–3 MW (1.5 s)	3600–7200 MW h (1.5 s)	Japan	Sumitomo Electric Ltd.
11	Not stated	170–275 kW	Not stated		
12	Not stated	Not stated	3.9 kW h	Australia	Not stated
13	Not stated	1 kW	50 kW h	Austria	ASFINAG (Austrian Motor and Expressway Operator)
14	77–78% 80–82%	≈ 1 kW (0.7–1.4 kW) ≈ 10 kW (5–10 kW)	Not stated 0.1 W h cm^{-2}	China	National 863 Program of China
15	Not stated	0.25–0.9 kW	24 W h dm^{-3}	China	Pan-tang Group Pang-zhi-hua Iron and Steel Research Institute
16	Not stated	80–150 W kg^{-1} electrolyte	2.5–10 MW h	Canada	VRB Power Systems Inc.

Table 3
Operational and environmental externalities reductions for the King Island 2500 kW wind farm/1100 kW RFB system (augmenting a 6000 kW diesel engine generator).
Reproduced with permission from Wiley [45].

Operational factor	Quantity	Annual value/$
Cost reductions		
Reduction of diesel spinning reserve operational time	8 h d^{-1}	91,500
Improved operational efficiency	25 dm^3 h^{-1} (spinning reserve)	83,200
Capture of 'spilled' wind power	1100 kW h d^{-1}	51,200
Maintenance reduction	12 fewer generator set run-hours d^{-1}	23,000
	Total	248,900
Emissions reductions		
CO_2	4 kton yr^{-1}	–
NO_x	99 ton yr^{-1}	–
Unburned hydrocarbons	75 ton yr^{-1}	–

There is still a utility-scale knowledge gap at both the executive and technical levels, leading to a predisposition towards continued investment in fossil fuels to support the increasing levels of renewable energy generation (e.g. in New Zealand [45]). As a consequence further research is essential to determine suitable electrolytes that can improve power density and overall storage efficiencies of RFBs so that the commercialization of the technology can be as economical and environmentally friendly as possible. At present RFBs employ some common types of electrolytes, which are discussed briefly below. Then a perspective is provided on the possible applications of ILs and DESs in RFBs after considering their current uses in several electrochemical engineering based processes.

3. Conventional electrolytes used in redox flow batteries and their drawbacks

Generally, most of the RFBs reported in the literature employ aqueous electrolytes. Therefore, their operating potential is constrained by the electrochemical stability window of water (depending on pH, generally lower than 2.0 V) [22]. Organic solvents offer a much higher potential window, e.g. 5 V for acetonitrile (CH_3CN), with which, much higher power and energy output can be obtained [33,52]. However, organic solvents tend to be detrimental to the environment due to high vapor pressures, toxicity and flammability.

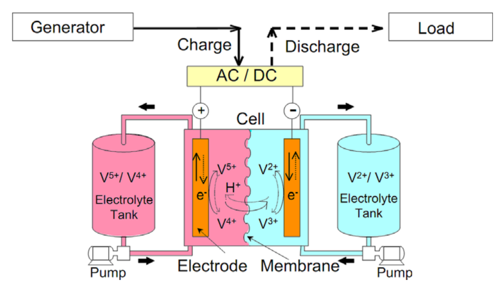


Fig. 3. Schematic of a vanadium redox flow battery and its working mechanism. Reproduced with permission from Electricity Storage Association [53].

3.1. Aqueous electrolytes

The most notable aqueous-based systems were the iron/chromium, the all-vanadium and the bromide/polysulfide technologies. The all-vanadium system achieved commercial fruition (Fig. 3) [1,53], while the other two faced limitations during scale-up [10]. Despite commercial success, the all-vanadium system suffered from some drawbacks such as high cost due to the ion-exchange membrane, low open-circuit potential leading to less power output and low energy density (ca. 25 Wh kg^{-1}) [1,7]. The problem of low energy density was tackled by inventing a vanadium/bromine redox system [54].

Preliminary studies were carried out with a 3–4 M vanadium–bromide solution in the negative half-cell and a 8–10 M HBr solution in the positive half-cell by Skyllas-Kazacos [54] followed by evaluation of membrane materials [1,55]. For this concentration of active ions, it was possible to reach energy densities up to 50 Wh kg^{-1} [55]. This cell showed a rapid loss of capacity due to the transfer of vanadium ions across the membrane into the positive half-cell solution [1]. To overcome this problem, vanadium–bromide was added to both half-cells, giving rise to the current G2 (second generation) V–Br cell

technology that employed the same electrolyte in both half-cells. As with the all-vanadium battery, the G2 V–Br also overcame the problem of cross contamination, but the higher solubility of vanadium halides compared with vanadium sulfate salts, allowed much higher energy densities to be achieved [1]. This technology was patented in 2008 [1,56]. Nonetheless, the potential concern of V–Br redox systems was the release of toxic bromine-vapor during operation. As a result, Skyllas-Kazacos [57] used bromine complexing agents such as tetra-butylammonium bromide, polyethylene glycol, N-methyl-N-ethyl morpholinium bromide, and N-methyl-N-ethyl pyrrolidinium bromide to decrease the hazards associated with the process [10]. A similar problem related to the toxic discharge of hydrogen sulfide gas was reported for the bromide/polysulfide system [58].

Despite the achievement of higher energy densities with the V–Br system, the problem of the electrochemical decomposition of water limited its potential power output. Due to this issue, researchers across the world considered the application of non-aqueous solvents as potential electrolytes in RFBs [52].

3.2. Organic electrolytes

The most common non-aqueous solvent employed as an electrolyte for RFBs was acetonitrile [20–24,59] as well as those used for uranium RFBs [60–62]. Open circuit cell potentials as high as 2.6 V were reported using acetonitrile but overall energy efficiency was limited to 40% [59]. In addition, the high cost of organic solvents and their high vapor pressures brought about a severe limitation to the system [52]. Due to these reasons, as well as concerns towards the safe handling of organic and flammable solvents, alternative non-aqueous solvents were required that could provide a high potential window of operation without carrying the inherent disadvantages of their organic counterparts [63]. In this regard, ionic liquids and deep eutectic solvents appeared to have some answers as discussed below.

4. Ionic liquids, deep eutectic solvents and their applications in electrochemical engineering based processes

Ionic liquids (ILs) are room temperature molten salts (that are liquid below 100 °C [64]), which have been used as solvents for many processes and as electrolytes in electrochemical devices [65,66]. Room temperature ILs (RTILs), being usually quaternary ammonium salts, are characterized by negligible vapor pressure, non-flammability as well as a broad electrochemical window (could be greater than 4 V). These compounds are liquid over a wide range of temperatures (down to −81 °C), possess high thermal and chemical stability as well as high density and electrical conductivity in comparison to other solvents [67,68]. Due to such advantages, ILs have enjoyed plenty of applications as electrolytes in sensors [69], electrochemical capacitors [70], lithium ion batteries [66], lead acid batteries [71], dye-sensitized solar cells [72] and fuel cells [73] amongst many others (Fig. 4) [74,75].

Several reviews are dedicated to the electrochemistry of ILs [75–80]. While ILs have many inherent advantages, issues such as complex synthetic steps [81], cost, lack of toxicity data and availability limit their practical use for large scale applications [80].

An alternative approach to simplifying the synthesis of ILs is to start with a straightforward quaternary ammonium halide and decrease the freezing point by complexing the anion to effectively delocalize the charge [82]. These mixtures form eutectics where the depression of freezing point can occur up to 200 °C. The use of simple amides, acids and alcohols as complexing agents makes the liquids very versatile and to distinguish them from other ILs the term deep eutectic solvents (DESs) is used [80,82]. These liquids have high conductivities, viscosities, and surface tensions (chemical structures of some typical components used to make DESs are

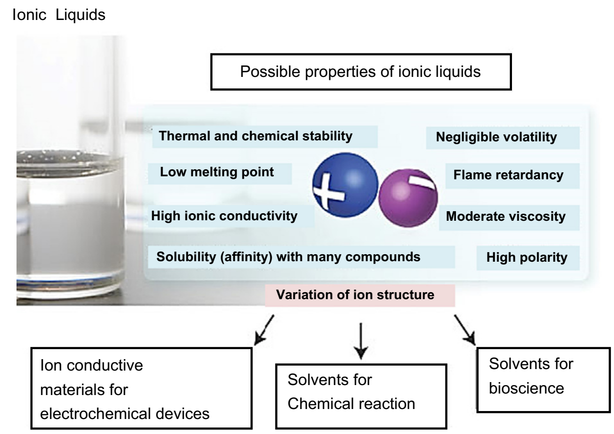


Fig. 4. ILs have various applications ranging from energy storage and conversion to metal deposition.
Reproduced with permission from the Nature Publishing Group [75].

given in Fig. 5 [63]). The fact that some of the hydrogen bond donors are commonly available as bulk commodity chemicals such as urea and oxalic acid gives them the potential for large-scale applications [82]. In addition, the primary advantages of DESs are the extremely low cost of the precursors and their general biodegradability [74]. Table 4 shows the commercial price of ILs synthesized at Queen's University Belfast [83] while Table 5 gives commercial rates for DESs prepared in the University of Leicester [84]. Clearly DESs can be manufactured at much lower costs than ILs. Hence, DESs have been used for electropolishing (Fig. 6) [85], shape controlled synthesis of gold nanoparticles (Fig. 7) [86,87], biodiesel purification (Fig. 8) [88,89] and metal oxide processing (Fig. 9) [90] applications successfully.

DESs are inferior to other ILs on a number of important points. Firstly, they have a much narrower window of electrochemical stability, which may limit their industrial electrochemical applications [74,91]. Secondly, they can exhibit significant volatility if the hydrogen bond donor molecule is, for instance, ethylene glycol. Despite these disadvantages, ILs and DESs have been used in many electrochemical processes, some of which are reviewed briefly below [74].

4.1. Electrochemical applications of ILs and DESs in metal processing

Ambient temperature ILs have been applied for the extraction of gold and silver from a mineral matrix [92]. Some work has also been carried out on the electrowinning of aluminum from ILs [93]. In the application of ILs and DESs to metal processing the major advantage is a significant reduction in the volume of aqueous streams required [94].

Some ILs have been designed to contain ions which are known to have lower toxicity than normal and these include functionalized imidazoles [95], lactams [96], amino acids [97] and choline [98]. It is only the last of these that have been extensively applied to metal processing [94].

Reline (a DES formed from a 1:2 mixture of choline chloride and urea) can be used to process the mixed metal oxide matrix from an electric arc furnace (Fig. 9) [99] while zinc and lead can be selectively removed and subsequently recovered from the liquid by electrowinning. Similarly Ethaline (a DES formed from a 1:2 mixture of choline chloride and ethylene glycol) facilitates metal dissolution in the electropolishing of steels [100]. Despite such progress, the underlying fundamentals of metal speciation and redox chemistry in high chloride media like DESs [101] are poorly understood. As a result an electrochemical series for metal ions in

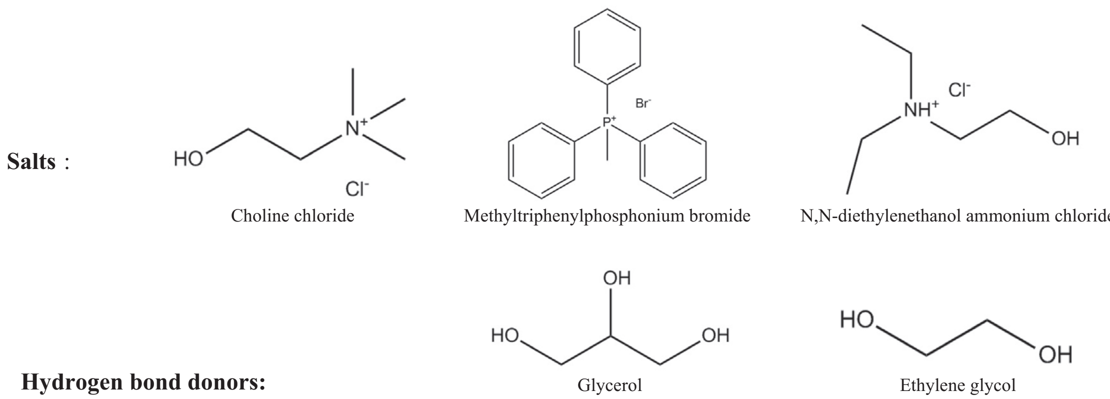


Fig. 5. Chemical structures of typical salts and hydrogen bond donors to synthesize DESs [31,63].

Table 4
Prices of some commercially available ionic liquids prepared at the Queen's University Belfast and sold by Acros Organics [83].

No.	Name of ionic liquid	Pack size (g)	Price (US$)
1	1-Butyl-2,3-dimethylimidazolium tetrafluoroborate	5	177.50
2	1-Butyl-2,3-dimethylimidazolium trifluoromethansulfonate	10	157.63
3	1-Butyl-3-methylimidazolium (L)-lactate	5	155.15
4	1-Butyl-3-methylimidazolium tetrafluoroborate	5	155.15
5	1-Butyl-3-methylimidazolium trifluoromethansulfonate	10	151.42
6	1-Butylpyridinium tetrafluoroborate	5	155.15
7	1-Butylpyridinium trifluoromethansulfonate	10	147.71
8	1-Decyl-3-methylimidazolium chloride	10	121.40
9	1-Dodecyl-3-methylimidazolium chloride	10	113.57
10	1-Ethyl-3-methylimidazolium (L)-lactate	5	145.22
11	1-Hexadecyl-3-methylimidazolium chloride	10	127.84
12	1-Hexyl-2,3-dimethylimidazolium tetrafluoroborate	5	182.46
13	1-Hexyl-2,3-dimethylimidazolium trifluoromethansulfonate	10	157.63
14	1-Hexyl-3-methylimidazolium hexafluorophosphate	25	118.84
15	1-Hexyl-3-methylimidazolium tetrafluoroborate	5	187.11
16	1-Hexyl-3-methylimidazolium trifluoromethansulfonate	10	141.50
17	1-Hexylpyridinium hexafluorophosphate	25	113.57
18	1-Hexylpyridinium tetrafluoroborate	5	180.00
19	1-Hexylpyridinium trifluoromethansulfonate	10	147.71
20	1-Octyl-3-methylimidazolium hexafluorophosphate	25	113.57

Table 5
Commercial prices of DESs manufactured in Leicester and sold throughout the UK [84].

Product description	Price (US$)/kg
Glyceline	313.29
Ethaline	313.29
Maline	391.61
Oxaline	313.29
Reline	313.29

DESs has been established to explain the similarities and differences from aqueous behavior [102].

Electrodeposition of metals from ILs became an area of periodic research from the 1930s onwards [103]. The first major breakthrough was the development of protic haloaluminate eutectics in the 1950s by Hurley and co-workers [104]. A further improvement was the development of the aluminum chloride and 1-methyl-3-ethylimidazolium chloride ($AlCl_3$ and EMIM-Cl) system in the 1980s [74]. The biggest drawback of chloroaluminate systems was their reactivity with water, which drastically limited their applications. Since the early 1990s attention was shifted to the use of other anions, for instance bis(trifluoromethyl)sulfonylamide $[N(CF\text{-}SO_2)_2^-]$, which resulted in liquids that were stable in the presence of air and water. An even better alternative to such ILs were several DESs for the electrodeposition of zinc–tin alloys [80] and copper [105] as explained below.



Fig. 6. Electropolishing unit used by Abbott and co-researchers [85]
Photo obtained with permission from Prof. K. Ryder, the University of Leicester, UK.

Type I eutectics was postulated by Abbott [106] to be the most suitable for depositing Al, Ga and Ge (four types of DESs have been defined in Table 6 [107,108]). Type II eutectics were considered most suitable for chromium deposition while Type III DESs were suited to Zn, Cu, Ag and associated alloys. Type III could also be applied in metal winning, oxide recycling and electropolishing [106]. In addition, the ability of Type III eutectics to replace environmentally hazardous chemicals such as CrO_3 and KCN together with the ability to fine tune the composition and morphology of alloys were considered as added advantages.

Electropolishing is the controlled corrosion of a metal surface to bring about a reduction in surface roughness (Fig. 6) [109]. The first systematic study of electropolishing was carried out by Jacquet in the 1930s [110]. The majority of studies have been carried out on stainless steel with a few focusing on copper, nickel and titanium [111–113]. While electropolishing is an extremely successful process there are major issues associated with the technology. The most notable drawback involves the use of a highly corrosive and toxic solution which results in extensive gas evolution during the process [109].

To solve this issue, eutectic mixtures of zinc, tin and iron halides with a variety of quaternary ammonium salts can be formed and

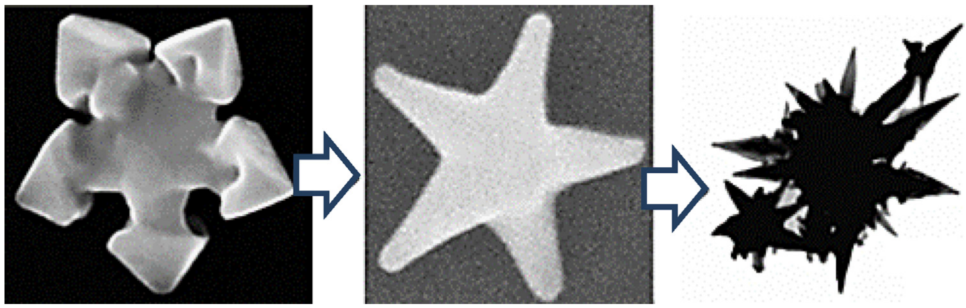


Fig. 7. The shape and surface structure of star-shaped gold nanoparticles (NPs) synthesized in the presence of DESs.
Reproduced with permission from Wiley [87].

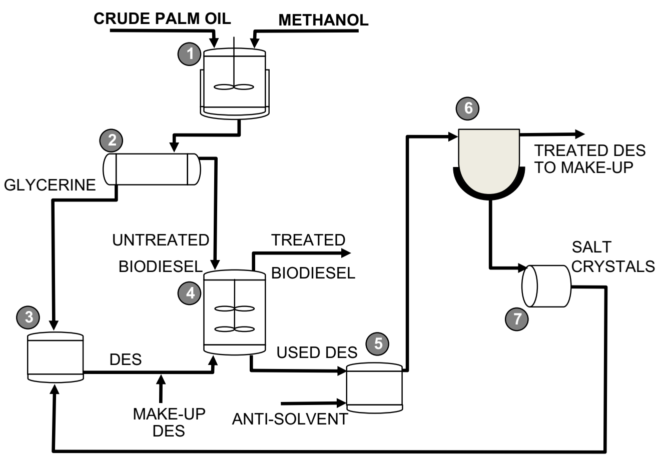


Fig. 8. Schematic of the purification of biodiesel: 1. Transesterification reactor, 2. decanter, 3. DES synthesis mixing tank, 4. extractor, 5. mixing tank, 6. crystallizer, and 7. rotating filter.
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used for metal finishing [98,114,115]. These DESs are air and moisture stable and the components are widely available and relatively benign. Zinc and its alloys can be electrodeposited with high current efficiency from these DESs [115]. This technology can be extended towards the electrodeposition and electropolishing of other metals by using hydrated metal salts [116,117].

Ethylene glycol can also be used as a hydrogen bond donor, and mixtures with choline chloride can be employed for the electropolishing of stainless steel [85]. This process is associated with high current efficiencies and negligible gas evolution at the anode/solution interface [109].

Other research groups have explored the possibility of applying choline chloride based DESs for the electropolishing of niobium [118]. It was reported that the addition of ammonium chloride to the urea–choline chloride eutectic could reduce surface roughness by more than 30% in comparison to that reported from standard HF–H_2SO_4 electrolytes.

Recently, metal nanoparticles stabilized by ILs have been synthesized with some unique properties [119]. Dupont and co-workers [120,121] reported that iridium nanoparticles stabilized by the imidazolium IL showed a large increase in activity for the biphasic hydrogenation of various olefins and arenes under mild reaction conditions [121]. Itoh et al. [122] synthesized AuNPs (gold nanoparticles) modified by an imidazolium cationic based IL. The IL-modified AuNPs could change color in aqueous solutions via anion exchange of the IL moiety [119]. Tatumi and Fujihara [123] reported that gold nanoparticles stabilized by a zwitterionic imidazolium sulfonate-terminated thiol exhibited a remarkably high stability in aqueous solutions with high concentrations of electrolytes, ILs, and proteins [119]. Metal nanoparticles, as discussed above, were all stabilized by small IL derivatives. Other workers [124] synthesized a gold-nanoparticle-containing an IL derived polymer by conducting the UV irradiation of 1-decyl-3-vinylimidazolium chloride in the presence of an aqueous solution of $HAuCl_4$ (chloroauric acid) [119]. A similar investigation but using a DES prepared from choline chloride and urea also reported the successful shape controlled synthesis of AuNPs (as shown in Fig. 7) [87]. In addition, the successful synthesis of silver [125], nickel [126], palladium [127], chromium, molybdenum, and tungsten nanoparticles [128] were reported in the recent past. Ag–Au alloy nano structures [129], TiO_2 nano tubulars [130], cobalt nano wires [131] and aluminum nanorods [132] were also prepared using ILs [133–137].

The synthesis of iron oxide nanoparticles (IONs) by the thermal decomposition of $Fe(CO)_5$ with stabilizers in the IL, [bmim][Tf_2N], was also reported [127,138]. ILs not only acted as stabilizing surfactants but also provided electrostatic protection for the synthesis of metal nanoparticles [139]. They also supported shape-regulating surfactants for the synthesis of anisotropic metal nanoparticles [140], such as CdS and ZnSe rods [141].

4.2. Destruction of halogenated hydrocarbons

Some recent patents are available describing the use of superoxide ions to destroy halogenated hydrocarbons (such as polychlorinated biphenyls or PCBs) in DESs [142–144]. First a stable superoxide ion is generated inside the ILs or DESs by the electrochemical reduction of oxygen. The superoxide ion is then used to destroy small quantities of various halogenated hydrocarbons, their homologous analogs and similar chemicals under ambient conditions [142,143]. The major advantage of this method is that no supporting electrolyte is necessary. Another invention reports on the generation of hydrogen peroxide (H_2O_2) in situ by using DES and the subsequent destruction of various halogenated hydrocarbons by means of the H_2O_2 [144].

Recently, the superoxide ion was intensively investigated by researchers using numerous solvents [145]. For ILs, generation of the superoxide ion by electro-reduction of O_2 in imidazolium chloride–aluminum chloride molten salt was reported by Carter et al. [146]. These researchers found that the generated superoxide ion was unstable and could not be utilized in reactions. In spite of this, AlNashef and co-researchers managed to stabilize the generated superoxide within the imidazolium based ILs in separate investigations [147–149]. This work was further extended to report the successful destruction of chlorobenzenes in ILs such as [$MOPMPip^+$][$TFSI^-$] {1-(3-methoxypropyl)-1-methylpiperidinium bis (trifluoromethylsulfonyl) imide} and [$HMPyrr^+$][$TFSI^-$] {1-hexyl-1-methyl-pyrrolidinium bis (trifluoromethylsulfonyl) imide} under ambient conditions [145].

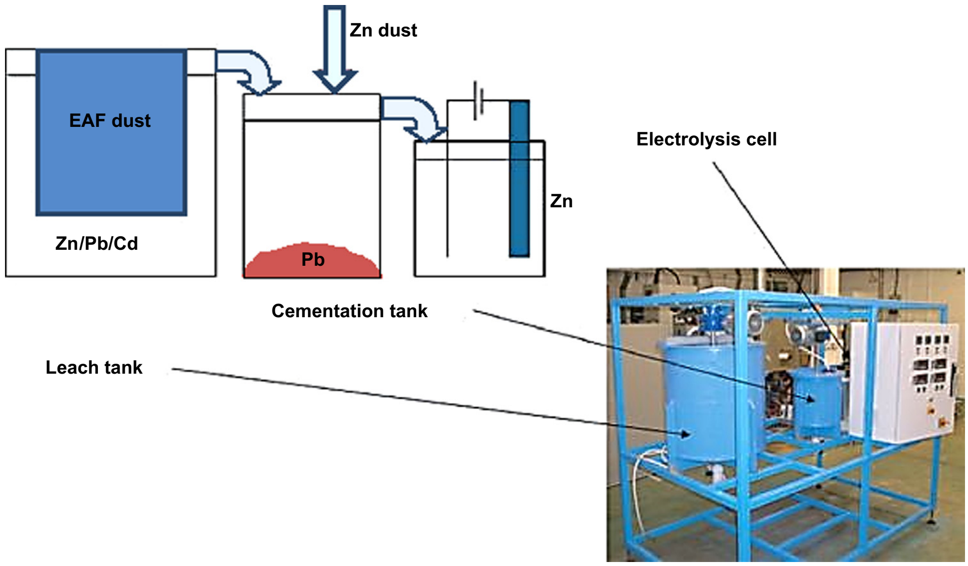


Fig. 9. Schematic of the cell for extracting lead and zinc from an electric arc furnace (EAF) dust together with a photograph of the pilot plant built for 5 kg dust extraction batches [89].
Reproduced with permission from Prof. K. Ryder, the University of Leicester, UK.

Table 6
Definition of four types of deep eutectic solvents (DES) [106–109].

Type of DES	General composition
Type I eutectic	Metal salt + organic salt (e.g. $ZnCl_2$ + choline chloride)
Type II eutectic	Metal salt hydrate + organic salt (e.g. $CoCl_2 \cdot 6H_2O$ + choline chloride)
Type III eutectic	Organic salt + hydrogen bond donor (e.g. choline chloride + urea)
Type IV eutectic	Metal salt (hydrate) + hydrogen bond donor (e.g. $ZnCl_2$ + urea)

4.3. Electrochemical energy storage applications

During the last few years there has been increasing interest in ILs as electrolytes for lithium or lithium-ion batteries (Fig. 10) [66,75]. The formation of the solid electrolyte interface (SEI) on the anode surface is critical to the correct operation of the system. ILs used as electrolyte components in Li-ion batteries are quaternary ammonium salts, such as those based on the tetraalkylammonium [R_4N^+] ion or cyclic amines that may be both aromatic (pyridinium, imidazolium) and saturated (piperidinium or pyrrolidinium) in nature. A good example of some typical ILs applied for Li-ion batteries is the *N*-butyl-*N*-methylpyrrolidinium bis (trifluoromethanesulfonyl) imide ($PYR_{14}TFSI$) [150,151]. $PYR_{14}TFSI$ is an air-stable, hydrophobic IL with very good thermal stability (up to 300 °C) as well as promising conductivity and viscosity at 20 °C (1.85 mS cm^{-1} and 95 mPa s, respectively) [152]. In addition, liquid imidazolium salts show stability of ca. 4 V, while piperidinium and pyrrolidinium or tetraalkylammonium salts, especially based on the imide anion, show stability at the level of ca. 6 V. Such stability is sufficient towards the use of ILs as electrolytes in Li-ion batteries [66]. There are no systematic studies on transport numbers of Li^+ containing ILs. This is a significant missing link in the literature as low values of lithium transportation numbers may lead to a concentration polarization of the battery.

LiTFSI/urea or lithium bis[(perfluoroethylene)sulfonyl]imide (LiBETI)/acetamide based DES binary systems display very low eutectic temperatures close to −37.7 °C and −57.0 °C, respectively [153]. In each case, the DES (e.g., those based on urea or acetamide) acts as a medium able to interact with both cations and anions in the solution. The DESs based on LiTFSI and acetamide are potentially promising electrolytes for electrochemical devices due to their excellent thermal stability, high ionic conductivity, broad electrochemical stability and low viscosity even at room temperature [154]. Indeed Li^+ cations coordinate with the C=O group of the acetamide (or urea) structure [155]. This interaction has been used effectively to determine the cycling performance of $LiFePO_4$, which demonstrates that the DES electrolytes do not react with the electrode surface in a Li ion battery. Also the discharge capacity ratio after 20 cycles at 80 °C is only 1% of the first discharge capacity with more than 99% efficiency.

The electric double layer capacitor (EDLC) is an energy storage device based on the operating principle of the electric double layer that is formed at the interface between an activated carbon material and an electrolyte (Fig. 11) [156–158]. This device stores electricity physically and lacks the chemical reactions found in rechargeable batteries during charging and discharging [157]. Various solvents and salts (solutes in other word) are available, offering specific advantages such as high capacitance and low temperature performances [158]. Generally, an organic electrolyte that is a solid quaternary ammonium salt, such as *N*,*N*,*N*,*N*-tetraethylammonium-tetrafluoroborate ($TEA-BF_4$), dissolved in propylene carbonate (PC, which has a high dielectric constant), has been used for high voltage EDLCs of 2 V or more. When compared to rechargeable batteries, the EDLC has a remarkably long cycle life and high power density [158,159].

ILs generally have high viscosity so that their ionic conductivity is lower than that of common organic electrolytes. This may cause a deterioration of power density in EDLCs [160]. The decrease in viscosity of ILs is, therefore, essential for improving the EDLC's performance. In the recent past, ILs based on imidazolium salts have been widely investigated because they have relatively low viscosity and high ionic conductivity [157,161–166]. For example EDLCs prepared with EMI-FSI [1-ethyl-3-methyl imidazolium bis (fluorosulfonyl)imide] show good performance despite the presence of a binder in an activated carbon-based electrode [160]. The self-discharge is suppressed by using the IL. A cycling durability test show that the cell with EMI-FSI keeps over 90% of the initial capacitance even after 10,000 cycles. Recently the application of a DES based upon 1-ethyl-3-methyl imidazolium bis(fluorosulfonyl) imide and N-methylacetamide (LiTFSI/MAc) has been reported as electrolytes for EDLCs [154]. The EDLC can be charged up to 2.5 V within a capacitance of an activated carbon electrode in this

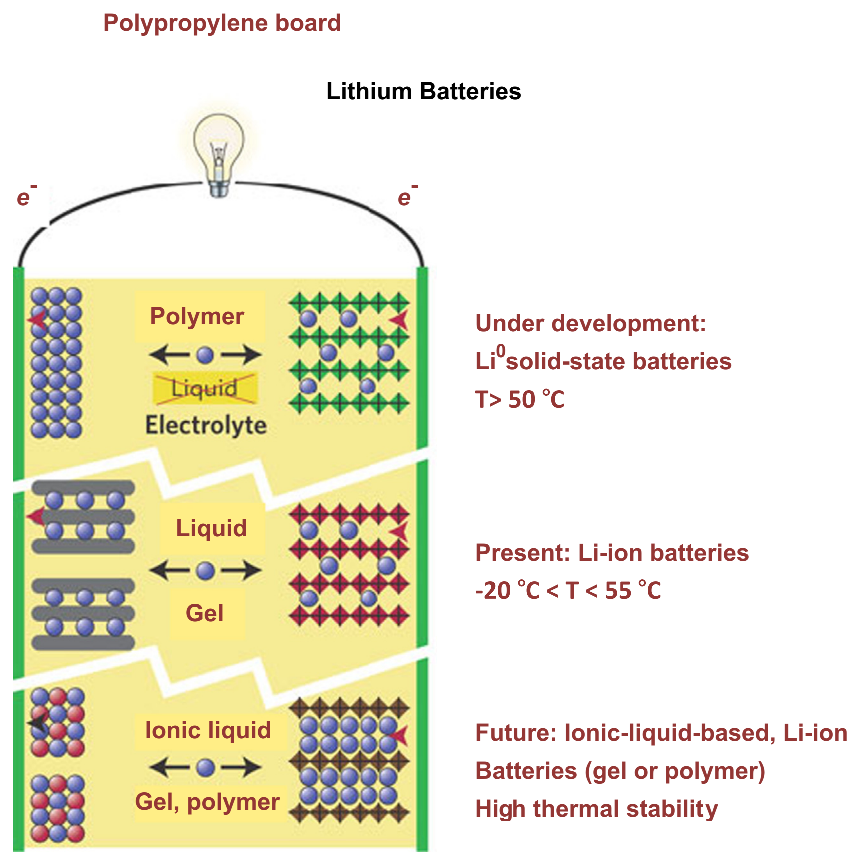


Fig. 10. A schematic showing how lithium batteries are formed by two lithium-exchanging electrodes separated by a lithium-ion-conducting electrolyte. Reproduced with permission from Nature Publishing Group [75].

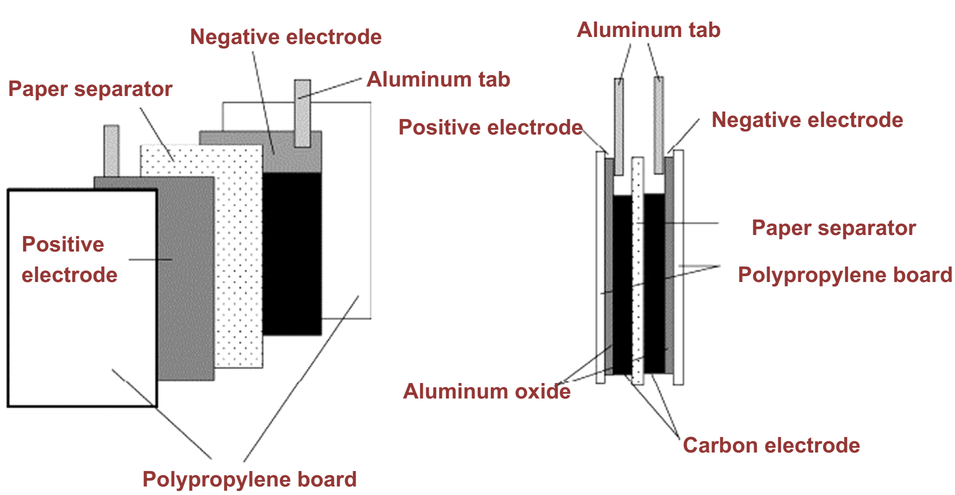


Fig. 11. EDLC test cell configuration.
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electrolyte to 152 F g^{-1}; this result is driven by the high dielectric constant value of MAc.

As low-volatility conductive media with good thermal stability, ILs are finding applications as fuel cell electrolytes and as proton conductors in proton exchange membranes, often in combination with polymer gels (Fig. 12) [167–169]. Typically, "protic" ILs, formed through the reaction of a strong acid with a base, is used as proton conductors. The first mention of an ammonium based DES serving as a component of a fuel cell electrolyte was by Matsui et al. [170] where a complex phosphate combination NH_4PO_3–TiP_2O_7 was used at 250 °C. Another investigation [171] reported on the operation of fuel cells in the temperature range of 100–200 °C (typical fuel cell operating range [172–174]) using similar ammonium based DESs. A later report [175] was based upon applying DESs to prepare phosphate-functionalized carbon monoliths as electrodes for supercapacitors. It was clear that the number of reports applying DESs for fuel cell applications were significantly lower than for ILs as discussed briefly below.

Several systematic studies on the use of ILs in fuel cells have been reported and promising results were obtained [176–178]. An

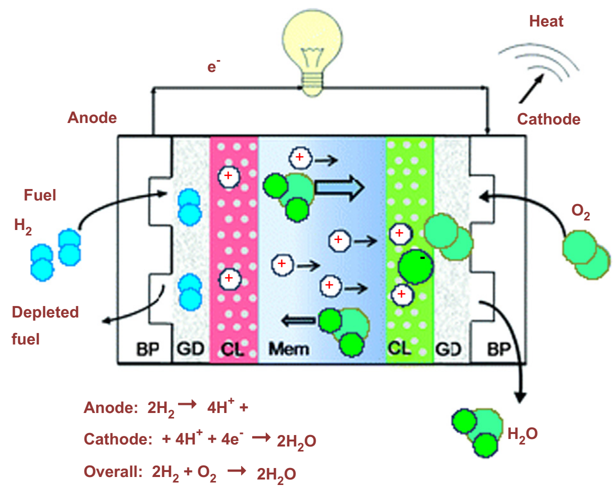


Fig. 12. Schematic diagram of a PEM fuel cell. BP, GD, CL and Mem represent bipolar plates, gas diffusion layers, catalyst layers and membrane, respectively. Reproduced with permission from Dr. R. Devanathan and the RSC [169].

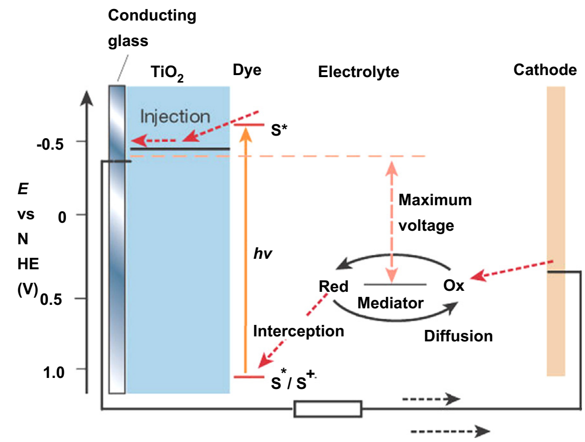


Fig. 13. Schematic of operation of the dye-sensitized electrochemical photovoltaic cell. Reproduced with permission from Nature Publishing Group [186].

efficiency of 67% was achieved using ILs such as 1-butyl-3-methylimidazolium tetrafluoroborate [BMI][BF_4] as electrolytes in an alkaline fuel cell [73] for instance.

Watanabe and co-workers show that some ILs are electro-active for H_2 oxidation and O_2 reduction under non-humidifying conditions [179]. In addition, some reports on utilizing ILs to substitute water in Nafion™ or directly as a liquid electrolyte for laboratory fuel cells are also available in the literature [73,180]. The use of IL aqueous solutions for wetting the membrane electrode assembly (MEA) used in fuel cells yield an impressive performance enhancement [181]. Compared with the classic polymer electrolyte membrane fuel cell (PEMFC), which uses only water on the polymeric membrane, the IL-PEMFC, using [BMI][BF_4] IL aqueous solutions, enhances the current density 50-fold, the power density 73-fold and increases the overall efficiency by 21% [73,181].

The application of ILs as membranes in fuel cells have also been reported [182]. For example polybenzimidazole membranes nano impregnated with phosphoric acid have been studied as electrolytes in PEMFCs for more than a decade [183]. Novel membranes consisting of an anhydrous proton solvent H_3PO_4, the protic IL propyl-3methylimidazolium di-hydrogen phosphate and polybenzimidazole (PBI) as a matrix have also been prepared and characterized for PEMFCs intended for operation at elevated temperatures (120–150 °C) [182]. More recently, several copolymers and related derivatives have attracted many researchers' attention, adding variety to the field [183]. Besides phosphoric acid, many other strong inorganic acids, as well as alkaline electrolytes have been used to impregnate benzimidazole membranes. However, phosphoric acid-doped PBI membrane-based fuel cells are not good for a pure hydrogen feed, and they provide inferior performance to that of Nafion-based fuel cells. Therefore they do not show much promise in comparison to perfluorosulfonic acid ionomer membranes, especially at temperatures less than 80 °C [184].

4.4. Dye sensitized solar cells (DSSCs) for renewable energy storage

Till now, ILs based on imidazolium salts have been widely used as solvents for DSSCs (Fig. 13) [72]. Unfortunately, pure imidazolium iodide/triiodide ILs are too viscous and obstruct the diffusion of the redox couple (I^-/I_3^-) in the electrolyte, thereby hampering device performance. The use of some binary IL electrolytes allows the reduction of electrolyte viscosity. It has been reported that ethylmethylimidazolium-based ILs with anions including tetracyanoborate ($B(CN)_4$), tricyanomethanide (TCM), dicyanamide (DCA) and thiocyanate (SCN) [185–189] appear to be promising for high performance DSSCs incorporating pure imidazolium iodide. Then again, their applications as electrolytes in DSSCs are limited by their high costs and toxicological issues [72,186]. The same is true for ether-functionalized imidazolium iodides due to their high viscosities and low conductivities [190]. Therefore, better alternatives are considered necessary for practical applications.

A eutectic mixture of glycerol and choline iodide (G.CI) was proposed and used as an electrolyte for DSSCs in a recent investigation [72]. Current–voltage characteristics of the G.CI/PMII (mixture of G.CI and 1-propyl-3-methylimidazolium iodide IL) based binary electrolytes stood at V_{oc} (open-circuit photovoltage)=0.533 V, J_{sc} (short-circuit photocurrent density)=12.0 mA cm^{-2} with a fill factor=0.582, and cell efficiency=3.88% under a light intensity of 100 mW cm^{-2}. Even better efficiencies in excess of 7% were reported recently using an IL based on acetyl imidazolium iodide and urea (DES) [191] as well as siloxane based cyclic sulfonium iodide gel type IL electrolytes [192]. Such improved results fare well for efficient conversion of the intermittent and yet renewable solar energy to useful electricity in future.

5. Applications of ionic liquids in redox flow batteries

A room temperature molten salt consisting of 1-ethyl-3-methylimidazolium chloride (EMICl) and aluminum trichloride ($AlCl_3$) was found to have low melting point and a wide electrochemical potential window for applications in RFBs [27]. A number of metal chlorides were found to dissolve in EMICl–$AlCl_3$ molten salt due to its adjustable Lewis acid–base property. Most of the soluble redox couples have been reported and studied under basic conditions [193–208] probably because the metal species of several high oxidation states were stabilized after forming chloro-complexes [27]. This fact was confirmed in a separate study whereby the Fe(III)/Fe(II) electron transfer process was irreversible in acidic ionic liquids, while this redox reaction became reversible in basic ionic liquids probably due to complex formation [209].

The standard formal potentials of the redox couples of various metal chloro-complexes were found to be distributed widely within the electrochemical potential window of a basic EMICl–$AlCl_3$ molten salt [27]. As a consequence, rechargeable RFBs having high cell voltages were envisaged by combining these redox couples in a basic EMICl–$AlCl_3$ molten salt. The redox reactions of some transition metals, such as iron, samarium, europium and ytterbium in BMPTFSI [BMP^+, 1-n-butyl-1-methylpyrrolidinium; $TFSI^-$, bis(trifluoromethylsulfonyl)imide] ionic liquid were investigated as the negative and

positive electrode reactions of the RFB [210,211]. Among these studies, it was found that the redox reactions of M(III)/M(II) (M = Fe, Sm, Eu and Yb) were quasi-reversible or irreversible when M(III) or M(II) was introduced into BMPTFSI by dissolving M(TFSI)*n* (*n* = 2 or 3) and that the diffusion coefficients of M(III) or M(II) were less than $\sim 10^{-7}\ cm^2\ s^{-1}$ [209]. These results suggested that the interaction between these metallic species and $TFSI^-$ anions led to the formation of complexes such as M*x*(TFSI)y^-, which caused slow electrode kinetics and low diffusivity. This complex formation was important for understanding the redox reactions of metallic species in BMPTFSI. With regard to bromo- and chloro-aluminate ionic liquids, it was reported that the electrochemical behavior of iron species was affected by the Lewis acidity of the ionic liquids [212–215].

In another study, the redox reactions of some lanthanides were examined as the candidates for the half cell reactions of the RFB using 1-ethyl-3-methylimidazolium and 1-n-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfone) imide (EMITFSI and BMPTFSI) molten salt systems [216]. Unfortunately, cyclic voltammetry indicated that the redox reaction of the Eu(III)/Eu(II) couple was irreversible electrochemically. The slow electrode kinetics may have been due to the formation of some complexes of Eu (III) probably with $TFSI^-$, which was suggested by UV–vis spectroscopy [1,216].

Very recently, Sandia National Laboratories have developed new types of metallic based ionic liquids for applications in RFBs [4]. The compounds consist of manganese, iron, cobalt, nickel, copper, zinc, or cerium coordination cations and weakly coordinating anions such as 2-ethylhexanoate, triflate, triflimide, or tetrafluoroborate that may simultaneously act as a solvent and electrolyte [217–219]. Most compounds are quite inexpensive to produce and some show promising viscosity, conductivity or electrochemical reversibility [4]. Theoretical calculations show that metal ion concentrations up to 6.5 M are possible in the ILs thereby opening up windows for future high energy density RFBs. New compounds are currently being developed and tested, and cell test data are forthcoming [220].

From preliminary investigations that considered the application of methylimidazolium iron chloride molten salt system in RFB applications [27], it was predicted that if a sodium chloride–sodium electrode was combined with this EMICl–$FeCl_2$–$FeCl_3$ molten salt, a high energy density per unit volume may be expected [1]. Since Na (I)/Na couple in EMICl–$AlCl_3$ system had the formal potential of −2.15 V at room temperature [28], the electromotive force of approximately 2 V was expected for the Na/EMICl–$FeCl_2$–$FeCl_3$ battery. Even though this battery appeared to have the advantage of a low operating temperature and a long cycle life compared with Na–S and Zebra cells [221], further work with this system appeared to be lacking in the literature. Instead recent work reported upon the application of 1-ethyl-3-methyl imidazolium hexafluorophosphate ILs as supporting electrolytes for organic RFBs (Fig. 14) [33]. The efficiencies obtained were not as good as those reported using standard supporting electrolytes such as tetrabutylammonium hexafluorophosphate. Further work on this topic has not been reported to date.

One reason for the lack of activity in the area of ionic liquids for RFBs is the fact that these materials are known to be sensitive to air and moisture, which makes their handling difficult in large-scale commercial applications [1,7]. These materials also tend to be quite expensive (as shown in Table 4) and are unlikely to be economically viable for RFB applications compared to the lower cost aqueous-based systems. In contrast, given the large electrochemical window of many ionic liquids, the possibility of using redox couples that fall outside the decomposition potential of water may open the way to the development of high voltage flow cells that offer much higher power and energy densities than current aqueous-based systems [1,7]. Further investigation of such

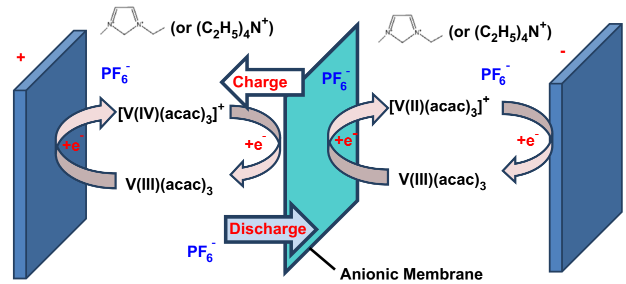


Fig. 14. A schematic representation showing the use of 1-ethyl-3-methyl imidazolium hexafluorophosphate ($EMIPF_6$) as supporting electrolytes in a RFB using acetonitrile solvent.
Reproduced with permission from Elsevier [33].

couples could therefore prove fruitful as long as practical systems can be shown to offer better performance, cell voltage and cycle life than the all-vanadium RFB to offset the high costs of these electrolytes.

6. Feasibility of using deep eutectic solvents for redox flow battery applications

The feasibility of applying DESs in RFBs can be ascertained from both economic and environmental impact analyses. It is obviously sensible to estimate the performance of recently reported DESs in RFBs [222,223] with that of the commercially developed vanadium RFB (VRFB) [224]. Assuming a typical 2 kW/30 kWh VRFB installation (as shown in Table 7) reported by Walsh [45], an economic analysis reveals an amortized capital cost of \$850 and a cost of stored electricity of[1] \$0.10 $kW^{-1}\ h^{-1}$. When the cost of electricity from wind power is added to the energy storage cost a total combined generation/storage cost of \$0.15–0.18 $kW^{-1}\ h^{-1}$ is obtained. From Table 5, it is clear that the commercial cost of the most commonly investigated DES, i.e., ethaline, is about an order of magnitude higher than that of the commonly available VRFB electrolyte (Table 7). However the future of VRFBs may not be very bright considering the high extraction costs of vanadium as displayed in Fig. 15 (the details for determining the figure has been explained in the literature [225]). For this reason, it is logical to develop simple, cost effective systems using materials exhibiting fewer supply constraint such as DESs [222]. In addition, a recent report has revealed that DESs are environmentally benign as they are produced naturally by plants and used for their metabolism processes [226]. Compare this with the environmental impacts of acidic based electrolytes that are normally applied in VRFBs. Therefore DESs show strong potential as future electrolytes for RFB applications.

So far, there have been two direct reports related to the study of redox species in DESs for applications in RFBs [222,223]. In addition, several DESs have been electrochemically characterized using redox couples such as ferrocene/ferrocenium [31,63], copper(II)/copper(I) [74] and other metallic ions in ethaline [102]. The rate kinetics of the copper(II)/(I) redox couple was shown to be appreciably higher in ethaline [74] in comparison to ionic liquids reported in the literature [105,227]. Similarly, the heterogeneous rate constant of ferrocene in DES [31] was of the same order of magnitude as in ionic liquids, determined recently [32,63,228,229].

The electrochemistry of DES is not severely affected if experiments are conducted in the open atmosphere [31]. This gives it an

[1] The analysis assumes operation and maintenance costs of \$0.008 $kW^{-1}\ h^{-1}$, a generous battery capacity factor of 50%, zero fuel costs, the exclusion of housing infrastructure costs, grid connection and a capital recovery factor of 0.13 at a 5% interest rate for a 10-year battery life expectancy [45].

Table 7
Estimated internal capital costs associated with a 2 kW/30 kW h all-vanadium redox flow battery.
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	Value	Cost per unit	Total cost
System data			
Mean current density	52 mA cm^{-2}	–	–
Electrode area	1.75 m^2 kW^{-1}	–	–
Flow cell costs			
Activated carbon-felt electrode	3.5 m^2 kW^{-1}	€50 m^{-2} ($70 m^{-2})	€350 ($490)
Bipolar current collector	–	€65 kW^{-1} ($91 kW^{-1})	€130 ($182)
Frame and associated components	–	€435 kW^{-1} ($609 kW^{-1})	€870 ($1218)
Ion-exchange membrane	2.1 m^2 kW^{-1}	€25 m^{-2} ($35 m^{-2})	€105 ($147)
Electrolyte storage tanks (× 2)	550 dm^3 (each)	€185 each ($259 each)	€370 ($518)
Pumps (× 2)	–	€160 each ($224 each)	€320 ($448)
Control system	–	€500 ($700)	€500 ($700)
Total flow cell cost	–	–	€2315 ($3241)
			€1157 kW^{-1} ($1620 kW^{-1})
Storage costs			
V_2O_5 (solute)	180 kg	€8.0 kg^{-1} ($11 kg^{-1})	€1440 ($2016)
Electrolyte manufacture	–	€3.0 kg^{-1} ($4 kg^{-1})	€540 ($756)
Tanks	550 dm^3 (each)	€185 each ($259 each)	€370 ($518)
			€2350 ($3290)
Total storage costs	–	–	€78 kW^{-1} h^{-1} ($109 kW^{-1} h^{-1})
			€4665 ($6531)
Overall internal cost	–	–	€155 kW^{-1} h^{-1} ($217 kW^{-1} h^{-1})

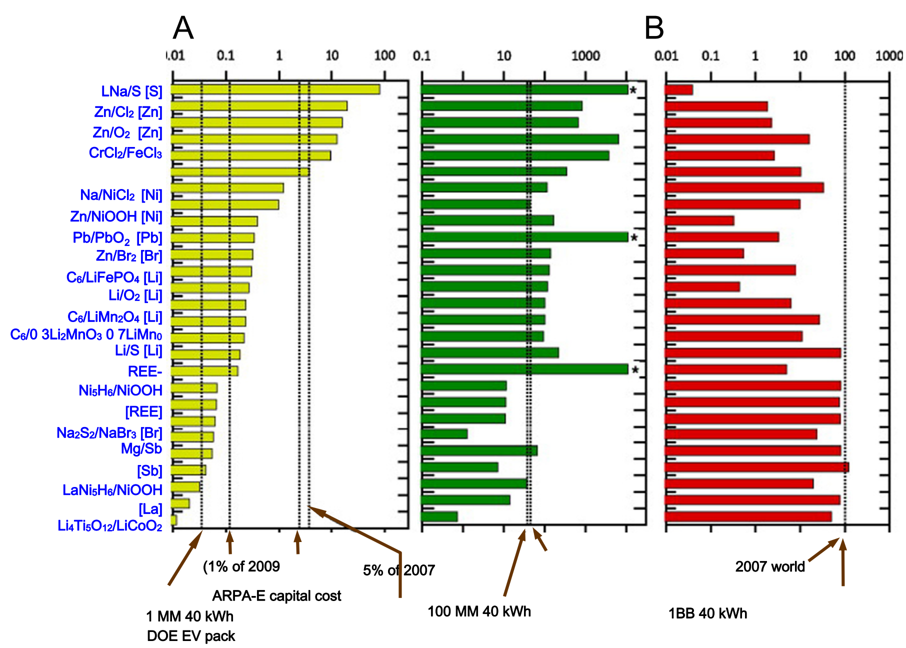


Fig. 15. (A) Energy storage potential (ESP) based on annual production of the elements. Short-term (10–15-year) and long-term (40–50-year) "flow" goals are provided for grid-storage and EV energy storage applications. The elements in brackets at the right side of the labels are the limiting elements in each couple. (B) ESP based on the reserve base of the elements. Long-term (40–50-year) "stock" goals are provided. **ESP well beyond the limit of the figure. (C) Extraction costs of the elements in the couples, calculated from the USGS prices of the elements.
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edge over acetonitrile or ionic liquids as solvents, because in most cases, non-aqueous electrolytes have been reported to undergo experiments under inert atmospheres (i.e., either purging the solutions with nitrogen or argon to remove dissolved oxygen and moisture or else experiments remain confined within expensive glove boxes) [24,227]. In addition, solubility of metal oxides based on vanadium, chromium, iron and zinc are reasonably high in DESs based upon urea or malonic acid, which shows some promise towards applications in RFBs [94]. Abbott and co-workers also report that the solubility of such metallic species can be improved in the presence of iodine as an electrocatalyst [102]. This would be extremely beneficial in improving the energy densities of RFBs running on DES-based electrolytes thereby encouraging their implementation in future electric vehicles.

In a nutshell, application of DES appears quite promising for RFBs due to the possibility of manufacturing the materials in bulk at reasonably low costs (Table 5) as well as due to the high heterogeneous rate constants of several metallic species in such solvents [63]. DESs can also be produced from different salts and hydrogen bond donors thereby adding versatility to the process (Fig. 5).

7. Conclusion

This work has reviewed RFBs for renewable energy storage and considered the applications of ILs and DESs as electrolytes for the system. ILs and molten salts have had plenty of electrochemical applications in the past and some have even shown potentials to be applied for RFBs. Despite that, the expense and complex synthetic steps for some ILs limit their practical application in RFBs. In contrast, DES has been reported to be manufactured from economical raw materials and is also biodegradable in nature due to which it can enjoy both bulk production and can also be labeled as an environmentally friendly solvent. Due to these reasons, electrochemical screening using ferrocene and other transition metallic species have been conducted showing that the electrode kinetics in DESs are similar to those reported for ILs. In addition, recent investigations have shown that it may be practical to implement copper or iron based RFBs using ethaline as the solvent as well as the supporting electrolyte. The aim of this review is to stimulate researchers in the area of RFBs to synthesize and apply other types of DESs as potential solvents using proven redox systems such as the all-vanadium and the bromine/polysulfide couples for efficient renewable energy storage. In that manner a possible commercial alternative may be discovered to the widely acclaimed aqueous-based VRFB.

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